

CLAIMS

1. A process for the polymerization of an ethylenically unsaturated monomer comprising:

a. providing a supported metallocene catalyst comprising a stereospecific metallocene catalyst component supported on a polyorganosilsesquioxane support comprising spheroidal polyorganosilsesquioxane support particles having an average particle size within the range of 0.3-20 microns and having an alkylalumoxane co-catalyst component supported on said polyorganosilsesquioxane support by reaction of said alkylalumoxane and said polyorganosilsesquioxane support; and

b. contacting said catalyst in a polymerization reaction zone with an ethylenically unsaturated monomer containing three or more carbon atoms or which is a substituted vinyl compound and maintaining said reaction under polymerization conditions to produce polymerization of said monomer to produce a stereoregular polymer.

2. The process of claim 1 wherein said polyorganosilsesquioxane support particles have an average particle size within the range of 5-15 microns.

3. The process of claim 1 wherein the polyorganosilsesquioxane powder is a polyalkylorganosilsesquioxane wherein the alkyl groups contain from 1-4 carbon atoms.

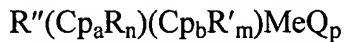
4. The method of claim 1 wherein said polyorganosilsesquioxane powder comprises polymethylsilsesquioxane and said alumoxane catalyst comprises methylalumoxane.

5. The process of claim 1 wherein said ethylenically unsaturated monomer is a C₃ or C₄ alpha olefin.

6. The process of claim 4 wherein said alpha olefin is propylene.

7. The process of claim 5 wherein said alkylalumoxane is at least partially supported on the outer surface of said polyorganosilsesquioxane particles.

8. The process of claim 1 wherein said metallocene is characterized by the formula:



wherein Cp_a is a substituted cyclopentadienyl ring, Cp_b is an unsubstituted or substituted cyclopentadienyl ring; each R is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R' is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R" is a structural bridge between the cyclopentadienyl rings imparting stereorigidity to the catalyst and is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; p is from 0 to 3, m is from 0 to 3, n is from 1 to 4; and wherein R'm is selected such that (Cp_bR'm) is a sterically different ring than (Cp_aR_n).

9. The process of claim 8 wherein R is selected such that (Cp_aR_n) forms a

substituted or unsubstituted fluorenyl group.

10. The process of claim 9 wherein Me is titanium, zirconium, hafnium, or vanadium.

11. The process of claim 10 wherein R" is a methylene, ethylene, organosilyl, substituted methylene, or substituted ethylene radical.

12. The process of claim 11 wherein R"(CpR_n)(CpR'_m) forms an isopropylidene (cyclopentadienyl-1-fluorenyl) radical or a diphenylmethylene (cyclopentadienyl-1-fluorenyl) radical.

13. The process of claim 10 wherein R is selected such that (Cp_aR_n) forms a substituted fluorenyl radical having bilateral symmetry and R' is selected such that (Cp_bR_m) forms an alkyl substituted or unsubstituted cyclopentadienyl radical having bilateral symmetry.

14. The process of claim 1 wherein R"(CpR_n)(CpR'_m) forms an isopropylidene (cyclopentadienyl-1-fluorenyl) radical or a diphenyl methylene (cyclopentadienyl-1-fluorenyl).

15. In a process for the polymerization of an ethylenically unsaturated monomer comprising:

a. providing a supported metallocene catalyst comprising a stereospecific metallocene catalyst component supported on a polyalkylsilsesquioxane support comprising spheroidal particles having an average particle size within the range of 0.3-20 microns and having an alkyl alumoxane cocatalyst component supported on said polyorganosilsesquioxane support by reaction of said alkyl alumoxane in said support to produce an oxygen linkage of said alkyl alumoxane to said support with the attendant production of trialkylaluminum; and

b. contacting said catalyst in a polymerization reaction zone with an ethylenically unsaturated monomer containing three or more carbon atoms or which is a substituted vinyl compound and maintaining said reaction under polymerization conditions to produce polymerization of said monomer to produce a stereorigid polymer.

16. The method of claim 15 wherein said ethylenically unsaturated monomer is a C₃-C₄ alpha olefin.

17. The method of claim 16 wherein said alpha olefin is propylene.

18. The method of claim 15 wherein said polyalkylsilsesquioxane powder comprises polymethylsilsesquioxane and said alumoxane catalyst comprises methylalumoxane.

19. The method of claim 18 wherein said catalyst includes trimethylaluminum.

20. In a process for the preparation of a supported metallocene catalyst comprising:

- a. providing a particulate catalyst support material in the form of a polyorganosilsesquioxane powder having an average particle size within the range of 0.3-20 microns;
- b. contacting said particulate support material with an alumoxane cocatalyst;
- c. providing a dispersion in an aromatic hydrocarbon solvent of a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures;
- d. mixing said metallocene solvent dispersion and the product produced by the reaction of said particulate catalyst support material and alumoxane for a period of time to allow said metallocene to become reactively supported on said particulate support to form a supported catalyst;
- e. recovering said supported catalyst from said aromatic solvent.

21. The process of claim 20 wherein the polyorganosilsesquioxane powder is a polyalkylorganosiloxane wherein the alkyl groups contain from 1-4 carbon atoms.

22. The method of claim 21 wherein said polyorganosilsesquioxane powder comprises polymethylsilsesquioxane and said alumoxane catalyst comprises methylalumoxane.

23. The method of claim 22 wherein procedures (a) and (b) recited in claim 20 involve the production of trimethylaluminum.

24. In a process for the preparation of a supported metallocene catalyst comprising:

- a. providing a particulate catalyst support material in the form of polyalkylsilsesquioxane powder having an average particle size within the range of 0.3-20 microns;
- b. contacting said particulate support material with an alkyl alumoxane cocatalyst to produce a reaction product of said polyalkylsilsesquioxane and said alkylalumoxane and a trialkyl aluminum;
- c. providing a dispersion in an aromatic hydrocarbon solvent of a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures;
- d. mixing said metallocene solvent dispersion and the reaction product produced by the reaction of said particulate catalyst support material and alumoxane for a period of time to allow said metallocene to become reactively supported on said particulate support to form a supported catalyst; and
- e. recovering said supported catalyst from said aromatic solvent.

25. The method of claim 24 wherein said polyalkylsilsesquioxane powder

comprises polymethylsilsesquioxane and said alkylalumoxane comprises methylalumoxane.

26. The method of claim 25 wherein procedures (a) and (b) recited in claim 20 involve the production of trimethylaluminum.

27. A supported metallocene catalyst composition comprising:

a. a particulate support comprising spheroidal polyorganosilsesquioxane support particles having an average diameter within the range of 0.3-20 microns and having an alkylalumoxane co-catalyst supported on the surface of said polyorganosilsesquioxane support by reaction of said alkylalumoxane and said polyorganosilsesquioxane support; and

b. a stereospecific metallocene supported on said particulate support and incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures.

28. The composition of claim 27 wherein said polyorganosilsesquioxane support particles have an average surface area of less than $100\text{ m}^2/\text{g}$.

29. The composition of claim 27 wherein said stereospecific metallocene catalyst component comprises at least two stereospecific metallocenes.

30. The composition of claim 27 wherein said stereospecific metallocene catalyst component comprises a syndiospecific metallocene.

31. The composition of claim 27 wherein said stereospecific metallocene catalyst component comprises an isospecific metallocene.